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(71) Applicant: CHEVRON RESEARCH COMPANY
525 Market Street
San Francisco California 94105(US)

(72) Inventor: Gordon, Chester D.
2579 Patra Drive
El Sobrante, CA 94803(US)

(72) Inventor: Fagan, Gian L.
45 Hillcrest
Benicia, CA 94510(US)

(74) Representative: Kosmin, Gerald Emmanuel et al,
HASELTINE, LAKE & CO. Hazlitt House 28 Southampton
Buildings Chancery Lane
London, WC2A 1AT(GB)

(54) Method of oxidatively degrading an olefinic polymer to produce an oxidised polymer product useful as a viscosity index improvement agent for a lubricating oil.

(57) A method of oxidatively degrading an olefinic polymer comprises oxidising the olefinic polymer in an inert solvent in the absence of molecular oxygen and in the presence of an oxidant mixture of at least one peroxide and at least one hydroperoxide, said oxidant mixture being present in an amount sufficient to effect molecular weight degradation and the mole ratio of peroxide to hydroperoxide being in the range from 3.2 to 1 to 0.4 to 1, whereby an oxidised polymer product is obtained. The oxidised polymers produced by this method can be further reacted with a nitrogen-containing compound such as a polyalkylene polyamine. The oxidised polymer products are of value as viscosity index improvement agents when incorporated in lubricating oil compositions.

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1 Method of oxidatively degrading an olefinic polymer
to produce an oxidised polymer product useful as a
viscosity index improvement agent for a lubricating oil

5 This invention relates to a method of oxidatively
degrading an olefinic polymer and to the use of the
oxidised polymer so-produced as a viscosity index
improvement agent in a lubricating oil composition.

10 An important property of a lubricant composition
is the rate at which its viscosity changes as a function
of temperature. The relationship between the viscosity
and temperature is commonly expressed in terms of the
viscosity index (V.I.). Lubricant compositions which
15 change little in viscosity with variations in temperature
have greater viscosity index than do compositions whose
viscosity is materially affected by changes in tempera-
ture. It is readily apparent, therefore, that one of the
major requirements of lubricating oils or other hydro-
carbon oil products is their satisfactory viscosity-tem-
20 perature characteristics. These characteristics are
necessary in order that the viscosity of the oil will not
become too low but will show an equally good performance
within a relatively wide temperature range to which it
may be exposed in service. The wider the possible
25 temperature variations, the smaller should be the change
in viscosity with temperature. Hence, the viscosity-
temperature characteristics of a lubricant which is used
in applications where wide variations in temperature are
encountered are of great importance and lubricant
30 compositions having high viscosity indices are highly
desirable.

 A variety of polymeric or high molecular weight
materials have been described as viscosity index
improvers for lubricants and have been prepared via an
35 air or oxygen sparging oxidation process which involves
the use of molecular oxygen in at least one step in the
preparation thereof. For example: U.S. Patent No.

1 3,417,020 teaches lubricating oil compositions of
improved viscosities containing degraded
ethylene-alpha-olefin polymers wherein the degraded
polymers have been hydroxylated. The hydroxylated
5 degraded polymers are prepared by hydroperoxidizing the
polymer with subsequent reduction of the hydroperoxide
groups to yield degraded products containing hydroxyl
groups and minor amounts of carboxyl, keto and aldehyde
groups.

10 U.S. Patent No. 3,756,954 teaches the preparation
of viscosity index improvers prepared by air oxidation of
interpolymers of ethylene and propylene in the presence
of an aliphatic amine.

British Patent Application No. 2,040,296A teaches
15 the preparation of a viscosity index improver additive by
oxidatively and mechanically degrading an ethylene
copolymer containing as one of its components from 0.05
to 3% of 2,5-norbornadiene.

U.S. Patent No. 3,316,177 teaches reaction of
20 polyamine with the reaction product of maleic anhydride
with an oxidized interpolpolymer of ethylene and propylene,
as a sludge dispersant in lubricant and fuel
compositions.

U.S. Patent No. 3,404,091 describes the prepara-
25 tion of nitrogen containing polymers, useful as sludge
dispersants and viscosity index improvers, by grafting
polar monomers such as acrylonitrile on to hydroperoxi-
dized ethylene-propylene copolymers.

U.S. Patent No. 3,687,849 describes the prepara-
30 tion of viscosity index improvers, pour point depressants
and dispersants, for fuels and lubricants, by grafting
various unsaturated monomers on to a degraded, oxidized,
interpolymer of ethylene and propylene.

U.S. Patent No. 3,687,905 describes the prepara-
35 tion of additives for fuels and lubricants by the
reaction of an unsaturated acid, such as maleic acid or
anhydride, with an oxidized, degraded interpolpolymer of
ethylene and propylene, followed by reaction with a

1 polyamine.

U.S. Patent No. 3,769,216 discloses the preparation of lube oil additives by the condensation of an amine with an oxidized ethylene-propylene copolymer, prepared by air blowing in the presence of a peroxide (also see U.S. Patent 3,785,980), or by mastication of the polymer in the presence of oxygen.

While not related to the preparation of viscosity index improvers, other oxygen-sparging oxidation methods applied to olefinic polymers are described in the prior art, for example, in U.S. Patent Nos. 3,153,025, 3,110,708 and 3,232,917.

With respect to these prior art methods, there is considerable concern about the safety aspects such as the possibility of an explosion using air oxidation of an olefinic polymer solution involving relatively large quantities of molecular oxygen and a large volume of hydrocarbon.

It has now been found in accordance with the invention that the oxidation of olefinic polymers is advantageously carried out in solution using a mixture of organic peroxide and hydroperoxide as the oxidizing agent. This system is preferred because it forms a single-reaction phase with the polymer solution, it is relatively non-corrosive, and it does not have the hazards associated with the air oxidation of hydrocarbons.

Thus in accordance with one aspect of the invention, there is provided a method of oxidatively degrading an olefinic polymer in the absence of molecular oxygen, which comprises oxidizing the olefinic polymer in an inert solvent in the presence of an oxidant mixture of at least one peroxide and at least one hydroperoxide, said oxidant mixture being present in an amount sufficient to effect molecular weight degradation and the mole ratio of peroxide to hydroperoxide being in the range from 3.2 to 1 to 0.4 to 1, whereby an oxidised

1 polymer product is obtained.

The oxidized polymer obtained by the foregoing method may be further reacted with one or more functional group-containing compounds, such as non-tertiary
5 nitrogen-containing compounds. Both the oxidized polymer and the functionalized derivatives thereof are viscosity-index improvement agents for lubricating oils. The polymers so produced also show excellent dispersancy properties in lubricating oils and have excellent
10 thickening power and shear stability.

The term "olefinic polymer" is used herein to mean polymers derived from olefinically unsaturated hydrocarbon monomers. The polymer may be a homopolymer, a copolymer, which term includes random, and block
15 copolymers, or a terpolymer or tetrapolymer, etc. Suitable homopolymers include polybutenes, such as polyisobutene having an \bar{M}_n in the range 5,000 to 60,000, preferably in the range 10,000 to 45,000. Suitable copolymers include ethylene copolymers, especially
20 copolymers of ethylene and a C_3 - C_8 alpha-olefin such as ethylene/propylene, e.g. ethylene/propylene copolymers containing from 20 to 65, preferably from 35 to 45 mole percent propylene and having an \bar{M}_n in the range 10,000 to 200,000, preferably from 20,000 to 70,000, and copolymers
25 of a vinyl aromatic monomer, e.g. styrene, alphas-methyl styrene or vinyl naphthalene, and a conjugated diene monomer, e.g. butadiene or isoprene, of which hydrogenated block copolymers containing from 10 to 40, preferably from 15 to 35 weight percent of the vinyl
30 aromatic monomer and having an \bar{M}_n in the range 25,000 to 125,000, preferably from 50,000 to 125,000, are preferred. Such polymers are described in, for example, U.S. Patents Nos. 3,994,815; 3,775,329; 3,668,125 and 3,763,044. Suitable random copolymers are described in
35 for example, U.S. Patents Nos. 3,554,911; 3,630,905; 3,752,767 and 3,772,169. Suitable terpolymers include terpolymers of ethylene, a C_3 to C_8 straight- or branched-

1 chain alpha-olefin, e.g. propylene, and a non-conjugated
acyclic or alicyclic diolefin, e.g. 1,4-hexadiene,
1,5-heptadiene, 1,6-octadiene, 1,4-cyclohexadiene, 5-
methylene-2-norbornene or 5-ethylidene-2-norbornene,
5 generally containing from 30 to 85, preferably from 40 to
70 mole percent ethylene, from 15 to 70, preferably from
30 to 60 mole percent alpha-olefin and from 0.5 to 20
mole percent, preferably from 1 to 15, even more
preferably from 2 to 10 mole percent diene and having an
10 \bar{M}_n in the range from 15,000 to 200,000, preferably from
20,000 to about 70,000. Preferred terpolymers are
terpolymers of ethylene, propylene and 1,4-hexadiene or
5-ethylidene-2-norbornene. Suitable tetrapolymers
15 include tetrapolymers of ethylene, a C_3 to C_8 straight-
or branched-chain alpha-olefin and two non-conjugated
acyclic or alicyclic diolefins. The preparation of the
terpolymers, using Ziegler-Natta catalysts, is described,
for example, in U.S. Patents Nos. 2,933,489, 3,000,866
and 3,093,621. These terpolymers and tetrapolymers,
20 which are primarily produced for use in elastomeric
compositions, are characterized by the absence of chain
or backbone unsaturation and contain sites of unsatura-
tion in groups which are pendant to or in cyclic
structures outside of the main polymer chain. It is an
25 advantage of the present invention that oxidation occurs
substantially on the main backbone chains of the polymers
in preference to the groups pendant to or outside the
backbone chain.

Mixtures of polymers may also be used, if so
30 desired, in the process of the invention. Thus blends
may be formulated to provide desirable properties, e.g.
improved low temperature thickening. Suitable mixtures
of polymers include mixtures of two or more ethylene/
propylene copolymers having different ethylene-propylene
35 ratios and/or molecular weights and mixtures of an
ethylene/propylene copolymer and a polyisobutene.

In accordance with the present invention, the

1 aforementioned olefinic polymers are employed as starting
materials in a controlled oxidation reaction using a
mixture of at least one peroxide and at least one
hydroperoxide referred to hereinabove as the oxidant
5 mixture. More specifically, the oxidized olefinic
polymers resulting from this invention are prepared by
dissolving the olefinic polymer in an inert solvent at a
temperature generally in the range of from 60°C to 250°C,
using agitation. A mixture of radical initiators is
10 added to the reaction medium under a pressure of from 0
to 1,000 psig (1 to 70.3 kg/sq.cm) and the reaction is
continued for a period of from about 0.05 to 20 hours.
There is essentially no introduction of oxygen from a
separate source into the reaction medium during the
15 oxidation reaction.

The final polymeric product may be recovered from
solution by evaporation of the solvent or by precipita-
tion with a non-solvent or by any other suitable method.
Alternatively, prior to removal of the inert solvent, a
20 lubricating oil may be added directly to the reaction
mixture and the inert solvent removed by vacuum
distillation.

The oxidized olefinic polymer can be made in batch
or continuous operation. In batch operation, the
25 individual components are added to a suitable reaction
vessel together or in discrete portions and dissolved in
an inert solvent. In continuous operation the reactant
or reactants are added continuously to a horizontal or
vertical reaction zone at appropriate feed rates in a
30 diluent or neat at temperatures to promote easy handling,
reaction and solubility.

The compositions of this invention have a thicken-
ing power in the range of from 10-35 cSt. "Thickening
power" as used herein is defined as the viscosity at
35 100°C of a neutral oil having a viscosity at 40°C of 28.6
cSt and at 100°C of 4.7 cSt, containing 2.8 weight
percent of the dry polymeric composition. Thickening
power is thus measured as an actual viscosity of the oil

1 due to incorporation of the polymer. Thickening power is
directly related to the molecular weight of the polymer,
but is used instead of molecular weight because of the
ease of measurement and greater practical significance of
5 data. While the thickening power of the compositions of
this invention may be broadly defined as being in the
range of 10-35 cSt, thickening power is more usually in
the range of 15-25 cSt.

The oxidation is carried out in the presence of a
10 mixture of at least one peroxide and at least one
hydroperoxide in a mole ratio of peroxide to hydroper-
oxide in the range from 3.2:1 to 0.4:1 and preferably in
the range from 1.7:1 to 0.8:1. Surprisingly, it has been
found that use of the combination is much more efficient
15 in oxidizing and degrading the olefinic polymer than the
use of either the peroxide or hydroperoxide alone.

Representative of the peroxides which may be used
in the mixture are, for example, cumene peroxide, dicumyl
peroxide, benzoyl peroxide, dilauryl peroxide, di(n-
20 propyl)peroxydicarbonate, tertiary butylperoxyisobuty-
rate, 2,5-dimethyl-2,5-di(t-butylperoxy) hexane and
acetyl cyclohexylsulfonyl peroxide. Representative of
the hydroperoxides which may be used are, for example,
cumene hydroperoxide, hydrogen peroxide, tertiary butyl
25 hydroperoxide and 2,5-dihydroperoxy-2,5-dimethylhexane.
It is also possible to use a single compound which
contains at least one peroxide group and at least one
hydroperoxy group, or a mixture of such compounds. The
concentration of the oxidant mixture relative to the
30 olefinic polymer in solution is generally in the range
from 1 to 20% by weight, preferably from 2 to 15 percent
and most preferably from 5 to 12% by weight.

The oxidation is carried out in a solvent
substantially inert to the reaction conditions. Solvents
35 such as toluene, xylene, hexane, or mineral neutral oils
can be used. Preferred solvents are benzene, chloroben-
zene and t-butylbenzene. The solvent may suitably be
present in an amount in the range from 20 to 99%,

1 preferably from 50 to 95%, and more preferably from 70 to 90% by weight, based on the weight of the olefinic polymer.

5 The oxidised polymer product obtained by the oxidation reaction is an oil-soluble product of lower molecular weight than the starting material. The molecular weight depends upon the extent and conditions employed during the oxidation reaction. Ultimately, the intermediate oxidized polymers are converted by oxidation
10 reactions to fragmented or degraded polymer materials containing carbonyl groups. The more vigorous the oxidation conditions and the longer the length of time maintaining such conditions, the greater the number of carbonyl groups introduced into the starting material.
15 It is sufficient, however, than on an average at least one carbonyl, preferably in the form of a carboxyl-carbonyl, is introduced into each molecule of the starting material.

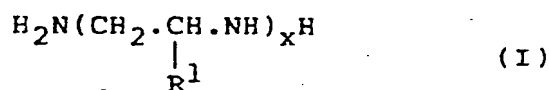
The oxidized polymer materials have a viscosity
20 average molecular weight of from about one-half to one-tenth of the molecular weight of the original material. The product of the oxidation process will generally have from 0.01% to 1% by weight oxygen and preferably from 0.2% to 0.8% by weight oxygen.

25 In accordance with another aspect of the invention there is provided a lubricating oil composition comprising an oil of lubricating viscosity and, as a viscosity index improvement agent, an oxidized olefinic polymer product containing carbonyl groups obtained by
30 the method of the invention as hereinbefore described. Preferably the polymer product is present in the lubricating oil in an amount of from 0.05 to 20% by weight.

It is believed that the majority of the carbonyl
35 groups introduced into the polymer, or at least the ethylene/propylene copolymers, by the oxidative method of the present invention tend to be carboxylic acid carbonyl groups rather than aldehydicarbonyl and ketocarbonyl

1 groups. Carboxylic acid carbonyl and ketocarbonyl groups
are favoured for the further chemical conversion of the
oxidized polymer. The oxidized olefinic polymers may be
reacted through their carbonyl groups with a variety of
5 other reagents, e.g., hydrogen or nitrogen, oxygen,
sulfur, boron and/or phosphorus-containing compounds to
form multifunctional products. It is preferred to react
the oxidized olefinic polymers with one or more nitrogen-
containing compounds (other than a tertiary nitrogen
10 compound), such as ammonia and organic amines which may
be mono, di or polyamines containing at least one primary
or secondary amino group, and, advantageously
polyalkylene polyamines having the general formula:

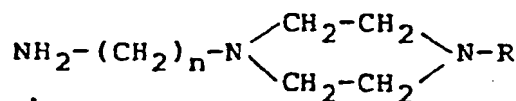
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wherein each R^1 is hydrogen or a C_1 to C_6 alkyl group,
20 preferably hydrogen, and x is an integer in the range
from 1 to 10, preferably in the range from 2 to 5, to
form a nitrogen-containing product having both viscosity
index improvement and dispersancy properties. Examples
of suitable nitrogen-containing compounds include 1,2-
25 diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane;
1,6-diaminohexane; diethylene triamine, triethylene
tetramine, tetraethylene pentamine; 1,2-propylene
diamine; di-(1,2-propylene) triamine, di-(1,3-propylene)
triamine and N,N-di-(2-aminoethyl) ethylene diamine.

30 Other polyamine compounds that may be used include
the N-aminoalkyl piperazines of the general formula:

35



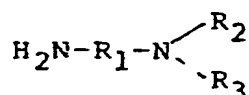
wherein n is from 1 to 3, and R is hydrogen or an

1 aminoalkyl radical containing from 1 to 3 carbon atoms. Specific examples include N-(2-aminoethyl) piperazine, N-(2-aminoisopropyl) piperazine and N,N'-di-(2-aminoethyl) piperazine.

5 The polyalkylene polyamines which may be used in the practice of this invention can be either pure alkylene amines or they can be commercial mixtures. For example, one process for preparing alkylene amines involves the reaction of an alkylene chloride such as
 10 ethylene chloride or propylene chloride with ammonia, which results in the production of somewhat complex mixtures of alkylene amines including various piperazines. One useful commercial product is a mixture of ethylene amines prepared by the reaction of ethylene
 15 chloride and ammonia and having a composition that corresponds to that of a tetraethylene pentamine. One such mixture is known in the trade under the name "Polyamine H".

Still other alkylene amino compounds that can be
 20 used include dialkylamino alkyl amines such as dimethylamino methyl amine, dimethylamino propyl amine, and methylpropylamino amyl amine. These may be characterized by the general formula:

25



wherein R_1 is an alkylene radical, e.g., an ethylene, propylene, or butylene radical, and R_2 and R_3 are C_1 to
 30 C_5 alkyl radicals.

Other useful amines include N,N-di-(2-hydroxyethyl)-1,3-propylene diamine; 3-dodecyloxypropylamine; N-dodecyl-1,3-propane diamine; tris-hydroxymethyl
 35 aminomethane, diisopropanolamine and diethanolamine. There may also be used the mono-succinimide, formed by reacting an alkenyl-succinic anhydride such as

1 polyisobutene succinic anhydride with either a diamine or
a polyalkylene polyamine having the formula (I).

The reaction conditions for the reaction of
carbonyl groups with nitrogen-containing compounds are
5 well-known in the art. Thus, for example, the
condensation of the oxidized rubbery polymers containing
a plurality of carbonyl groups and preferably carboxylic
acid carbonyl groups with a primary or secondary amine to
an aminated carbonyl compound useful as a lubricating oil
10 additive is carried out in the presence of a
substantially inert solvent at a temperature generally of
from 100°C to 280°C for a period of generally from 1 to
24 hours. Typical solvents include the hydrocarbon oil
into which the product is designed to be incorporated.
15 Alternatively, another solvent miscible in the
lubricating oil and liquid at the reaction temperature
may serve as the reaction medium. This would include
aromatics such as mixed xylenes, as well as aliphatic
oils and halogenated materials such as o-dichlorobenzene.
20 The mole ratio of polyamine to oxidized polymer is
generally in the range from 0.2 to 2.5 moles of amine per
mole of oxidized polymer.

Methods for preparing aminated polyolefins are
described for example in U.S. Patents Nos. 3,785,980;
25 4,132,661 and 4,317,772.

In a similar manner other preferred derivatives of
the oxidized olefinic polymers which are useful as
viscosity-index improvers may be formed by reaction with
(1) reducing agents or hydrogen to form hydroxylated
30 polymers are described in U.S. Patent No. 3,388,067,
which hydroxylated polymers may be further reacted with
isocyanates as described in U.S. Patent No. 3,404,092,
(2) oxygen-containing compounds such as maleic anhydride
followed by reaction with a polyamine as described in
35 U.S. Patents Nos. 3,687,905 and 3,316,177 and (3) sulfur
compounds or sulfur compounds and an amine as described
in U.S. Patents Nos. 4,317,738 and 4,320,017.

1 It will be appreciated that the invention includes
within its scope a lubricating oil composition comprising
an oil of lubricating viscosity and, as a viscosity index
improvement agent, a further-reacted and functionalized
5 oxidized olefinic polymer product as described above.
Preferably the polymer product is present in the
lubricating oil in an amount of from 0.05% to 10% by
weight.

 The lubricating oils used in the compositions of
10 the invention are oils of lubricating viscosity, and
particularly of the type useful in internal combustion
engines and can be predominantly paraffinic or
naphthenic, or they can be a mixture of both types of
mineral oils, as well as synthetic oils which include
15 polymers of various olefins, generally of 10 carbon atoms
or higher, and alkylated aromatic hydrocarbons. In
general, the lubricating oil will preferably be a
relatively highly refined mineral oil of predominantly a
paraffinic nature and will have a viscosity in the range
20 of from 2 to 20 cSt at 100°C.

 Other additives, such as detergents, rust
inhibitors, anti-oxidants, anti-wear agents, etc., may
also be present in the lubricating oil composition.
These other additives will be present in conventional
25 concentrations. Preferred additives which may be present
in the lubricating oil composition in effective amounts,
and preferably in the concentration range of from 0.01%
to 5%, include neutral and overbased alkali and alkaline
earth metal sulfonates or phenates or combinations
30 thereof, a metal dihydrocarbyl dithiophosphate such as a
zinc dialkyl dithiophosphate and/or an alkenyl succini-
mide or succinate or mixtures thereof.

 The invention is illustrated by the following non-
limitative Examples.

35

Example 1

A pipe reactor consisting of 7.62 m of 12.7 mm
carbon steel pipe heated by steam tracing was used for

1 this reaction. A solution containing 8% by weight of an
ethylene/propylene/1,4-hexadiene terpolymer (a product
manufactured by Du Pont Company, Wilmington, Delaware,
USA and sold under the trade name Ortholeum 2038, which
5 is a terpolymer having about 60 mole percent ethylene
groups, 39 mole percent propylene groups and 1 mole
percent 1,4-hexadiene groups and having a molecular
weight of about 250,000) in chlorobenzene was first
pumped through a hot oil heat exchanger and heated to a
10 temperature of 167°C. The solution was then fed into the
reactor at 340 g/min. The reactor was kept at 155°C
using steam and the pressure was maintained at 200 psig
(14 kg/sq.cm). At the front end of the reactor two other
solutions were pumped in - a 50% by weight dicumyl
15 peroxide in chlorobenzene at 2 ml/min. and an 8% by
weight hydrogen peroxide in water at 8 ml/min. At the
end of the reactor 100 Neutral oil was line mixed with
the reaction mixture at 272.4 g/min.

50 gallons (0.189 m^3) of the reaction mixture
20 containing oil was stripped in a 100 gallon (0.379 m^3)
glass kettle at 300°F (148.9°C) and 20 mm Hg for 1 hour.
Then, it was transferred to a 50 gallon (0.189 m^3)
stainless steel kettle and stripped at 400°F (204.4°C)
and 20 mm Hg for 1 hour.

25 The final product has the following properties:
Viscosity at 100°C (9.75% polymer product by weight)=
281.6 cSt
Viscosity of 2.8% solution in 100 N oil = 17.0 cSt
(Thickening Power)

30 Example 2

The product of Example 1 was line mixed with a
3.7% solution of ethylene diamine (EDA) in C₇₋₉ aromatic
hydrocarbon solvent mixture. The polymer solution was
pumped at 133.5 ml/min. and the EDA solution was pumped
35 at 33.4 ml/min. The total mixture was then fed into a
wiped film evaporator kept at 450°F (232.2°C). The
stripped product was filtered through a 100 μ filter and

-14-

1 had the following properties:

Flash Point = 390°F (198.9°C)

Viscosity at 100°C (9.75% by weight product) =
426.4 cSt

5 Viscosity of 2.8% solution in 100 N oil = 20.7 cSt
(at 100°C)

Nitrogen content = 149 ppm.

Multi-grade lubricating oils with good dispersancy
and shear stability were prepared using the product of
10 this Example.

Example 3

A pipe reactor consisting of 7.62 m of 12.7 mm
carbon steel pipe heated by steam tracing was used for
this reaction. A solution containing 8% by weight of the
15 ethylene/propylene/1,4-hexadiene terpolymer used in
Example 1 in chlorobenzene was first pumped through a hot
oil heat exchanger and heated to a temperature of 216°C .
The solution was then fed into the reactor at 0.8 lb/min.
(0.36 kg/min). The reactor was kept at 188°C using steam
20 and the pressure was maintained at 200 psig (14.06
kg/cm²). At the front end of the reactor two other
solutions were pumped in - a 6.25% by weight dicumyl
peroxide in chlorobenzene at 2 ml/min. and a 25% by
weight cumene hydroperoxide in chlorobenzene at 9.2
25 ml/min. At the end of the reactor 100 Neutral oil was
line mixed with the reaction mixture at 0.36 lbs/min
(0.16 kg/min).

50 gallons (0.189 m³) of the reaction mixture
containing oil was stripped in a 100 gallon (0.379 m³)
30 glass kettle at 300°F (148.9°C) and 20 mm Hg for 1 hour.
Then it was transferred to a 50 gallon (0.189 m³) stain-
less kettle and stripped at 400°F (204.4°C) and 20 mm Hg
for 1 hour.

The final product had the following properties:
35 Viscosity at 100°C (15% polymer product by weight) =
2111 cSt
Viscosity of 2.8% solution in 100 N oil = 19.8 cSt

1 (Thickening Power).

The above-mentioned product was line mixed with a 3.75% solution of ethylene diamine (EDA) in C₇₋₉ aromatic hydrocarbon solvent mixture. The polymer solution was pumped at 133.5 ml/min. and the EDA solution was pumped at 33.4 ml/min. The total mixture was then fed into a wiped film evaporator kept at 450°F (232.2°C). The stripped product was filtered through a 100 μ filter and had the following properties:

10 Flash Point = 300°F (148.9°C)

Viscosity at 100°C (15% by weight product) = 2558 cSt

Viscosity of 2.8% solution in 100 N oil = 20.5 cSt (at 100°C)

15 Nitrogen content = 98 ppm.

Multi-grade lubricating oils with good dispersancy and shear stability were prepared using the foregoing product of this Example.

Example 4

20 Eighty grams of the ethylene/propylene/1,4-hexadiene terpolymer used in Example 1 was dissolved in 920 g of chlorobenzene at 110°C with stirring. The solution was cooled to about 25°C after which a mixture of cumene hydroperoxide and dicumyl peroxide, in the mole ratios shown in Table I below, were added thereto with mixing. The reaction mixture was pumped at 19.7 g/min into a 50 ml reactor tube (a one quarter inch (6.35 mm) stainless steel tubular reactor) which was maintained at 180°C and 200 psig (14.06 kg/cm²). The residence time in the reactor was 2.75 minutes.

30 To 500 g of the reacted mixture were added 267 g of 100 Neutral oil. The chlorobenzene was removed from this mixture by distillation at 200°C and 20 mm Hg pressure yielding a 15% by weight solution of the oxidized polymer in oil.

A portion of the final product solution was then diluted to 2.8% by weight polymer using additional 100

1 Neutral oil. The viscosity of the resulting 2.8% solution at 100°C in centistokes is what is defined as Thickening Power (TP).

5 The data in Table I demonstrates the effect of varying the mole ratio of peroxide to hydroperoxide on the thickening power of the oxidized polymer.

TABLE I

10	Run No.	Moles		Mole Ratio of Peroxide to Hydroperoxide	TP*
		Dicumyl Peroxide	Cumene Hydroperoxide		
	1	0.33	0.07	4.7:1	44
	2	0.30	0.13	2.3:1	28
	3	0.27	0.18	1.5:1	20
	4	0.22	0.26	0.8:1	21
15	5	0.19	0.33	0.6:1	27
	6	0.15	0.40	0.4:1	32
	7	0.11	0.46	0.2:1	37
	8	0.07	0.53	0.1:1	58

20 *TP for starting polymer before oxidation was about 45 cSt

Example 5

To 4000 grams of a chlorobenzene solution containing 8% by weight of the ethylene/propylene/1,4-hexadiene terpolymer used in Example 1 were added 12.7 grams of cumene hydroperoxide and 29.7 grams of dicumyl peroxide with mixing. The reaction mixture was pumped at 33 g/min. into a 50 ml reactor tube (a one quarter inch (6.35 mm) stainless steel tubular reactor) which was maintained at 200°C and 200 psig (14.06 kg/cm²). The residence time in the reactor was 1.5 minutes.

To 500 grams of the reacted mixture were added 118.13 g of 100 Neutral oil. The chlorobenzene was removed from this mixture by distillation at 200°C and 20 mm Hg pressure.

A portion of the final product solution was then diluted to 2.8% by weight polymer using additional 100

- 1 Neutral oil. The viscosity (Thickening Power) of the resulting 2.8% solution at 100°C was 12.7 cSt. The oxygen content of the product as determined by Neutron Activation Analysis was 0.33%. The acid content was
- 5 2.8 mmole COOH/100 g polymer and the hydroxyl content was 0.069 mmoles OH/100 g polymer.

Multi-grade lubricating oils with good dispersancy and shear stability were prepared using the product of this Example.

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Example 6

- Lubricating oil compositions in accordance with this invention was evaluated in the standard Sequence V-D automotive engine test. In the Sequence V-D test, lubricants containing the experimental additives are
- 15 charged respectively to a standard internal combustion engine. The engine is operated at an assigned load and temperature, and at the end of a prescribed time the engines are disassembled and examined for deposits and wear. This engine test is a standard method well known
 - 20 in the industry.

Also, viscosity measurements at 100°C, 40°C and 0°C show acceptable viscosity measurements and with the use of pour point depressants, acceptable viscosity measurements at -32°C are obtained.

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A. Standard Sequence V-D Engine Test

- Formulated 10W-30 oils (Exxon 150 neutral) containing the viscosity index improvement additives shown in Table I were prepared and tested in a Sequence V-D Test method phase 9-2 (according to candidate test
- 30 for ASTM) as shown in Table II below. This procedure utilizes a Ford 2.3-litre four-cylinder engine. The test method simulates a type of severe field test service characterized by a combination of low speed, low temperature "stop and go" city driving and moderate
 - 35 motorway operation. The effectiveness of the additives in the oil is measured in terms of the protection provided against deposits and valve train wear. Each of

1. the formulated 10W-30 oils also contained 3.5% of a polyisobutenyl succinimide (50% by weight concentrate in oil), 20 mmoles/kg overbased calcium sulfonate, 30 mmoles overbased magnesium sulfonate, 18 mmoles dialkyl dithiophosphate, 0.3% dialkyl diphenylamine and 1% of a sulfonate-succinimide reaction product overbased with potassium triborate.

TABLE II
Sequence V-D Performance

10	Average <u>Formulation</u>	Piston <u>Sludge</u>	Average <u>Varnish</u>	Cam Lab Wear		
				v. 10^{-3} <u>Varnish</u>	inch <u>Avg.</u>	<u>Max.</u>
	1.1% Product of Example 1	9.5	8.0	8.4	0.4	0.6
15	1.1% Product of Example 2	9.1	7.9	8.0	0.5	0.7
	1% Product of Example 3	8.6	7.8	7.7	0.5	0.8
	0.7% AMOCO 6565 ¹	9.4	8.1	7.3	0.6	0.7
20	0.7% TLA 555 ²	9.1	7.7	8.0	0.5	0.7

¹Commercial VI Improver - vinyl pyrrolidone grafted on to an ethylene/propylene copolymer.

²Commercial VI Improver - oxidized ethylene/propylene copolymer reacted with formaldehyde and an amine.

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1 CLAIMS:

1. A method of oxidatively degrading an olefinic polymer, which comprises oxidizing the olefinic polymer in an inert solvent in the absence of molecular oxygen and in the presence of an oxidant mixture of at least one peroxide and at least one hydroperoxide, said oxidant mixture being present in an amount sufficient to effect molecular weight degradation and the mole ratio of peroxide to hydroperoxide being in the range from 3.2 to 1 to 0.4 to 1, whereby an oxidised polymer product is obtained.
2. A method according to Claim 1, wherein the olefinic polymer is a copolymer of ethylene and a C_3-C_8 alpha-olefin.
3. A method according to Claim 2, wherein the olefinic polymer is an ethylene-propylene copolymer.
4. A method according to Claim 1, wherein the olefinic polymer is a terpolymer of ethylene, a C_3-C_8 alpha-olefin and a non-conjugated acyclic or alicyclic diolefin.
5. A method according to Claim 4, wherein the olefinic polymer is a terpolymer of ethylene, propylene and 1,4-hexadiene.
6. A method according to any preceding claim, wherein the oxidizing reaction is carried out at a temperature in the range from 60 to 250°C and under a pressure of from 0 to 1,000 psig (1 to 70.3 kg/cm²).
7. A method according to any preceding claim, wherein the oxidant mixture is present in an amount of from 1 to 20% by weight, based on the olefinic polymer.
8. A method according to any preceding claim, wherein the hydroperoxide in said oxidant mixture is hydrogen peroxide, cumene hydroperoxide, tertiary butyl hydroperoxide, or 2,5-dihydroperoxy-2,5-dimethylhexane, and the peroxide in said oxidant mixture is dicumyl peroxide, benzoyl peroxide, or dilauryl peroxide.

- 1 9. A method according to Claim 8, wherein the
oxidant mixture comprises hydrogen peroxide and dicumyl
peroxide.
10. A method according to Claim 8, wherein the
5 oxidant mixture comprises cumene hydroperoxide and
dicumyl peroxide.
11. A method according to any preceding claim and
further comprising reacting the oxidised polymer product
with an organic amine containing at least one primary or
10 secondary amino group.
12. A method according to Claim 11, wherein the
organic amine is a polyalkylene polyamine having the
general formula:
- $$\text{H}_2\text{N}(\text{CH}_2\text{CHR}^1\text{NH})_x\text{H}$$
- 15 wherein each R^1 is hydrogen or a C_1 to C_6 alkyl group and
 x is an integer in the range of from 1 to 10.
13. A method according to Claim 12, wherein the
amine is ethylene diamine.
14. An oxidised polymer product obtained by the
20 method claimed in any preceding claim.
15. A lubricating oil composition comprising an oil
of lubricating viscosity and, as a viscosity index
improvement agent, an oxidised polymer product as claimed
in Claim 14.

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